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# A Further Investigation of the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

## Dissertation.

Submitted to the Board of University
Studies of the Johns Hopkins University
for the Degree of Doctor of Philosophy.

– by –
William E. Henderson.

1897

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# Acknowledgment.

The author esteems it a privilege as well as a pleasure to give expression to his sincere sense of gratitude to Prof. Remsen, under whose guidance this work was carried on, not only for instruction received in the lecture room, but for his frequent suggestion, and his constant and friendly interest in the work as it progressed. These have at all times been an encouragement and an incentive.

He wishes also to express his appreciation of the instruction and kindly guidance in the laboratory, of Drs. Morse and Renouf, as well as of Dr. Ames of the Physical Laboratory.

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# I. Introduction.

The sulphobenzoic acids have been the subject of investigation in this laboratory for a number of years past. Among the many interesting facts that have been brought to light in the course of this study, perhaps no others have been attended with more interest than the discovery of well characterized isomerism in the case of the chlorides of orthosulphobenzoic acid, and its paranitro derivative; together with the preparation of a series of isomeric derivatives of these substances. The chlorides themselves have been isolated in crystalline condition, and have been found to differ markedly.

not only in chemical, but in physical properties as well

The first evidence that such isomerism existed, was obtained by Remsen and Coates[1] who, in the course of an investigation of the action of aniline upon the chloride of orthosulphobenzoic acid, obtained two isomeric anilids quite different in properties, which they designated as fusible and infusible respectively. The following year, Remsen and Kohler[2] obtained one of the chlorides in crystalline form, together with an oil which they did not succeed in crystallizing.

This however was accomplished the succeeding year by Remsen and Saunders[3], and a still more satisfactory result was obtained by Remsen and McKee[4] in 1895. The chloride melting at 79°

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1 Am. Chem. Journ. XVII-311.
2. Ibid XVII, 330
3. Ibid XVII 354
4. Ibid XVIII, 794

was found to yield only the fusible anilid, together with an anil, while from the lower melting chloride, in addition to these, the infusible anilid was also formed.

In 1895, Gray[1] isolated the two corresponding isomeric chlorides of paranitro-orthosulphobenzoic acid, the lower melting chloride being obtained in small quantity only. The succeeding year Hollis[2] made a more careful study of this lower melting chloride, and prepared it in considerable quantity.

From evidence drawn from the action of ammonia upon these chlorides, taken in connection with a number of other facts, the higher melting chloride is identified as the one possessing a symmetrical structure,

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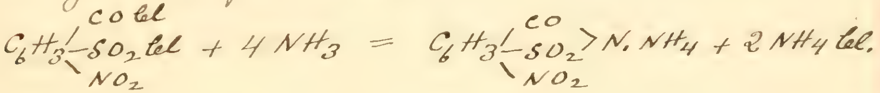
1. Inaug. Diss. J. H. Univ. 1895.
2. Inaug. Diss. J. H. Univ. 1896.

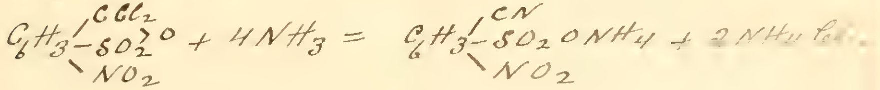
while the lower melting chloride possesses an unsymmetrical structure. The first one, when treated with ammonia is slowly transformed into the ammonium salt of paranitrobenzoic sulphinide:



$$C_6H_3\begin{array}{l}/COCl\\-SO_2Cl\\\backslash NO_2\end{array} + 4NH_3 = C_6H_3\begin{array}{l}/CO\\-SO_2\end{array}\!\!>N.NH_4 + 2NH_4Cl.$$

$$\phantom{C_6H_3}\backslash NO_2$$

while the lower melting chloride is quickly transformed into the ammonium salt of paranitroorthocyanbenzene-sulphonic acid:



$$C_6H_3\begin{array}{l}/CCl_2\\-SO_2\\\backslash NO_2\end{array}\!\!>O + 4NH_3 = C_6H_3\begin{array}{l}/CN\\-SO_2ONH_4\\\backslash NO_2\end{array} + 2NH_4Cl.$$

Gray's study of the symmetrical chloride was confined for the most part to the preparation of a series of salts of this latter acid, and to an investigation of the action of aniline upon

the chloride itself. It was thought to be of interest to extend this study to a wider range of reactions, as well as to improve, if possible, the method of preparing the chloride in pure condition. At the suggestion of Prof. Remsen this work was accordingly undertaken.

## II Preparation of Material.

The method employed in the preparation of paranitroorthosulphobenzoic acid was essentially that described by Hart[1] Kastle[2] Gray[3] and Hollis[4]. The details of it are repeated here for the purpose of calling attention to certain facts that came under the authors notice.

100 grams of paranitrotoluene are added to 400 grams of fuming sulphuric acid, and the mixture heated in a balloon flask at 100° on a water bath. The heating is continued until a few drops of the mixture, added to cold water, dissolves completely to a clear solution. The time required for this operation varies much with the

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[1] Am. Chem. Journ. I, 350

[2] Ibid XI, 177.

[3] Inaug Diss. J. H. Univ. 1895

[4] Inaug Diss. J. H. Univ. 1896

conditions. Continued stirring very considerably hastens the reaction, as paranitrotoluene forms a layer on the acid, which presents a small surface to its action. With constant stirring the reaction is complete in a few hours, whereas if no stirring is resorted to, as much as several days may be required, especially when large quantities are employed at one time.

When the reaction is complete, the mixture is poured into a large volume of water, and neutralized with calcium carbonate. In the filtrate from calcium sulphate, the calcium salt of paranitro-orthotoluene sulphonic acid is found, and this is converted into the potassium salt in the usual way.

The oxidation of the potassium salt

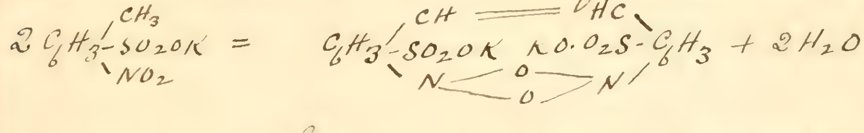
is effected as follows. 50 grams of the salt are dissolved in 2½ litres of water, and to this is added a solution of 15 grams of potassium hydroxide. The mixture is heated to 100° on a water bath, and when this temperature is reached, 110 grams of potassium permanganate are added. Heating is continued until the solution is decolorized, care being taken to prevent the evolution of free oxygen.

The oxides of manganese are then filtered off, the filtrate neutralized with hydrochloric acid, and evaporated to about one fifth of its original volume. Strong hydrochloric acid is then added in excess, and on cooling the acid potassium salt of paranitroorthosulphobenzoic acid separates in very slender colorless needles completely filling the liquid.

For the success of this operation it is important that the potassium salt of paranitroorthotoluenesulphonic acid and the potassium hydroxide should both be perfectly dissolved before they are heated together. If the two substances lie together in solid form at the bottom of the flask, a very slight elevation of temperature leads to the formation of an extremely troublesome red substance which is very difficult to remove. It is almost impossible to remove it from the oxidation product by recrystallization, since any considerable amount of it has a marked influence on the solubility of the salt, rendering it much more soluble. It persists throughout all subsequent transformations of paranitroorthosulphobenzoic acid, and should therefor be

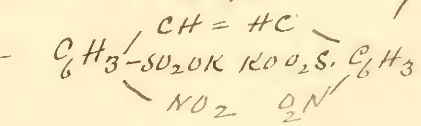
carefully avoided.

Otto Fischer[1] has shown that in concentrated solution, potassium hydroxide acts on nitro derivatives of toluene, with the formation of various colored substances derived from stilbene. In the case of paranitro orthotoluenesulphonic acid, he describes the substance formed as possessing a cherry red color. The reactions involved in its formation are:



$$2\,C_6H_3\begin{cases}CH_3\\ SO_2OK\\ NO_2\end{cases} = C_6H_3\begin{cases}CH = \\ SO_2OK\\ N<^{O}_{O}>\end{cases}\begin{matrix}HC\\ KO.O_2S\\ N\end{matrix}\!\!\!\!\begin{matrix}\\ C_6H_3\\ \\ \end{matrix} + 2H_2O$$

By oxidation this passes to a nitro compound of the composition



$$C_6H_3\begin{cases}CH = \\ SO_2OK\\ NO_2\end{cases}\begin{matrix}HC\\ KOO_2S.\\ O_2N\end{matrix}C_6H_3$$

It was no doubt the formation of substances of this nature that occasioned the color observed in some of the oxidations.

The only effective method of separating

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[1] Ber. XXVI - 2231; XXVIII - 2281

this colored substance was found to be, to pass to the neutral salt of paranitro ortho sulphobenzoic acid, by making the solution slightly alkaline. The salt of this colored substance is also formed and the two can be separated by a few recrystallizations in a fairly satisfactory manner.

The yield in both of the transformations involved in the preparation of paranitroorthosulphobenzoic acid, does not fall far short of the theoretical.

## III. Preparation of the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

This chloride was first separated from its unsymmetrical isomer by Gray[1]. It was obtained by allowing a chloroform solution of the mixed chlorides to evaporate until the chloroform had almost entirely disappeared. In the thick liquid so obtained, crystals of the symmetrical chloride were formed. It was also obtained by applying the method devised by Bucher in connection with the corresponding chloride of ortho-sulphobenzoic acid i.e. by the action of dilute ammonia on the mixed chlorides[1]. Gray also found that the best conditions for securing a relatively large proportion of the symmetrical chloride were, the employment of as low

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1. Inaug. Diss. J. H. Univ. 1895

a temperature as possible in the formation of the chlorides, and of as small an excess of phosphorus pentachloride as would suffice for the reaction.

After many experiments, under widely differing conditions, the following method of procedure, embodying the results of Gray's work, was adopted.

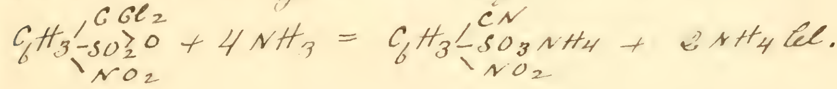
Dehydrated acid potassium salt of paranitro orthosulphobenzoic acid, and phosphorus pentachloride, in the ratio of 40:55 grams are brought together in a mortar and intimately mixed. The mixture is put into an evaporating dish, and placed on a sulphuric acid bath, previously heated to 150°. As soon as the action has been well started, the dish is removed, and the reaction allowed to proceed without further heating. When it is

complete, and the contents of the dish has cooled down to the temperature of the room the oily product is poured slowly into a salts bottle containing ice water, the bottle being frequently shaken during the process. The shaking is continued with renewed portions of water, as long as the wash water is cloudy. The water is then poured off, the brownish gummy chloride dissolved in chloroform, and the solution placed in a good sized separating funnel. Ice water is then added, and the contents of the funnel treated with successive portions of ammonia (desk ammonia diluted one half). Shaking is continued after each addition until the odor of ammonia has disappeared, and ice is added from time to time as may be required.

When it is found that the odor of

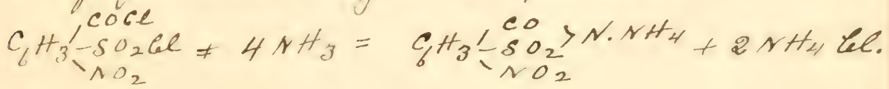
ammonia persists after several minutes' shaking, the chloroform layer, which is usually filled with a solid substance that has separated during the process, is drawn off, filtered, and dried with calcium chloride.

By this process all of the unsymmetrical chloride is converted into the ammonium salt of paranitroorthocyanbenzenesulphonic acid, according to the equation:



$$C_6H_3\begin{cases}\left.\begin{array}{l}CCl_2\\ SO_2\end{array}\right\rangle O\\ NO_2\end{cases} + 4NH_3 = C_6H_3\begin{cases}CN\\ SO_3NH_4\\ NO_2\end{cases} + 2NH_4Cl.$$

while the symmetrical chloride remains for the most part unchanged, though some of it is converted into the ammonium salt of paranitrobenzoic sulphinide:



$$C_6H_3\begin{cases}COCl\\ SO_2Cl\\ NO_2\end{cases} + 4NH_3 = C_6H_3\begin{cases}\left.\begin{array}{l}CO\\ SO_2\end{array}\right\rangle N.NH_4\\ NO_2\end{cases} + 2NH_4Cl.$$

It was found that working in this way

the symmetrical chloride could be prepared in pure condition, free from its isomer. The chloroform completely evaporates in a short time leaving fine crystals of the symmetrical chloride. In case the evaporation is slow and incomplete, it may be concluded that not all of the unsymmetrical chloride has been removed. The yield was uniformly about 40 per cent of the theoretical.

From the water used to wash the chlorides a considerable amount of the original salt can be recovered, as the reaction under the conditions employed, is never complete.

An examination was made of the substance mentioned as separating in the chloroform solution of the chlorides, during the treatment with ammonia, and

it was found to possess the following properties. It is insoluble in benzene, chloroform, acetone, ether and ligroin; soluble in glacial acetic acid, from which it separates on cooling in colorless, crystalline condition; is soluble in the cold in water, alcohol and ammonia, but by boiling with these reagents, or by long standing in the cold, it is dissolved with decomposition. It was dissolved in hot water and the solution, which was acid in reaction, was neutralized with potassium carbonate. On adding an excess of hydrochloric acid to the solution, and allowing it to cool, characteristic crystals of acid potassium salt of paranitroorthosulphobenzoic acid separated. These properties identify the substance as the anhydride of this acid

The formation of the corresponding anhydride of orthosulphobenzoic acid by the action of phosphorus penta chloride upon its acid potassium salt was observed by Solon[1], who made use of the reaction to prepare this anhydride in quantity.

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[1] Inaug. Diss. J.H. Univ. 1896.

## IV. Properties of the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

As first obtained, the crystals of the symmetrical chloride resemble irregularly shaped pieces of amber, both in color, and in lustre. On recrystallization from chloroform or ether, they may be obtained perfectly colorless, and are often of very simple crystallographic form. The chloride crystallizes in the monoclinic system, and possesses a very remarkable crystallizing power, in which respect it differs noticeably from its isomer. Even in chloroform solution that is far from dry, crystals appear with the greatest ease.

The habit of the crystals differs very much according to the conditions of crystallization. Not infrequently almost perfectly formed

crystals of the simplest form - the oblique octahedron - were obtained though for the most part the form was much more complicated, pinacoid and dome faces, together with basal planes being prominent. As a rule, the crystals were not suitable for crystallographic work, as the faces are usually uneven and the edges rounded. By proper precautions however, good ones were obtained, and measurements of these will be found in this dissertation when it appears in print.

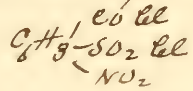
The size of some of the crystals obtained was unusual for substances of this class. One crystal, obtained with no special precautions, save letting a solution of the chloride stand undisturbed for several days, in a rather cool place measured 3 × 2.5 × 1.5 C.M., and weighed 11.2 grams.

The crystals are quite compact, their density being about 1.85. They melt at 98° (uncorr.) The chloride is quite stable in crystalline condition. Even in moist air the crystals were unchanged, and retained their lustre as long as they were in my possession.

An analysis for chlorine gave the following results.

.2200 gram gave .2212 gram AgCl.

Cal. for



$C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases}$

Found.

Cl = 24.94 24.83

## V. The Action of Benzene and Aluminium Chloride on the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

Hollis[1] in his study of the action of these reagents upon the unsymmetrical chloride, tested their action upon one portion of the symmetrical chloride, and found ~~finding~~ the products to be identical in the two cases. A few experiments were made in confirmation of these results, and the same products, in general, were obtained. It was observed however that the reactions differ in the relative ease with which they are brought about. In the case of the symmetrical chloride, the reaction is a much more vigorous one. On adding aluminium chloride to a solution of the symmetrical chloride in benzene, action begins

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Inaug. Diss. J. H. Univ. 1896.

at once at the temperature of the hand, and very little external heat, and that only in the latter stages of the operation, is needful for the completion of the reaction. The application of much heat converts all of the product into thick tarry substances from which nothing satisfactory could be obtained.

When the reaction was complete, the resulting product was isolated and purified in accordance with the directions given by Hollis. Repeated trials showed that, as in the case of the unsymmetrical chloride, only one phenyl group could be introduced by this method. The resulting compound, paranitro ortho benzoyl-benzene sulphon chloride, was identical with that derived from the unsymmetrical chloride. Owing, however, to the

fact that so much more decomposition occurs in the reaction with the symmetrical chloride, the paranitroorthobenzoyl benzene sulphon chloride could not be obtained in perfectly pure condition. In appearance it agreed closely with that described by Hollis, forming very characteristic greenish, rhombic crystals. These melted, not very sharply, at 174° instead of 177° as observed by Hollis.

Accordingly, to establish the identity of the two compounds beyond any doubt, the material on hand was converted into the barium salt of paranitro orthobenzoylbenzene sulphonic acid. This was done by boiling the sulphon chloride with dilute hydrochloric acid until complete solution had been effected; evaporating to dryness on a water-bath; dissolving

the residue in hot water, and neutralizing with barium carbonate. On filtering the hot solution from the excess of carbonate, and allowing it to cool, the barium salt separated.

The solution was somewhat colored by impurities, and the long needles in which the salt crystallized were also somewhat colored. They were analysed with the expectation that they would prove to be specimens of the salt described by Hollis as having three, or three and a half molecules of water of crystallization, in as much as the conditions under which they were formed were favorable to the formation of salts with these ratios of water of crystallization. Hollis found that this salt could be obtained with at least four different ratios of water of crystallization

viz. three, three and a half, six and seven molecules respectively. The analysis was as follows, the amount of barium being calculated on the basis of the anhydrous salt.

0.3087 gram lost 0.064 gram at 210° and gave 0.0759 gram $BaSO_4$

| Cal. for $(C_{13}H_8O_6NS)_2Ba + 11H_2O$ | Found |
|---|---|
| $H_2O$ = 20.90 | 20.73 |
| Ba = 18.29 | 18.23 |

The mother-liquor, in which the crystals remaining from analysis were redissolved, was warmed but not boiled, with bone black, to remove impurities. When filtered, the solution was perfectly colorless, and on standing for some time, well formed colorless, rhombic crystals appeared. On analysis they gave results as follows.

0.2804 gram lost 0.0405 gram at 210°, and gave 0.0736 gram $BaSO_4$

| Cal. for $(C_{13}H_8O_6NS)_2Ba+7H_2O$. | Found. |
|---|---|
| $H_2O = 14.40$ | 14.44. |
| $Ba = 18.29$ | 18.03 |

In making a further supply of the salt it was found that if the solution, after filtering from the barium carbonate, was diluted to such an extent that no crystals separated on cooling, then on slow evaporation under a bell jar the first crystals to appear were very long slender needles. As evaporation proceeded, these needles became much thicker assuming prismatic proportions, and corresponded in appearance to the salt described by Hollis as having six molecules of crystal water. As growth proceeded, the crystals became dark in color, and the mother liquor correspondingly clearer, the crystals evidently absorbing the impurity in their growth.

when the solution had become quite colorless, rhombic crystals of the salt containing seven molecules of water of crystallization appeared. The larger prismatic crystals were carefully removed, and redissolved in water in order to see if the same phenomena would repeat themselves. This in fact was the case, crystals of both types appearing in the same way as described. Without separating the crystals in this second experiment, water was added, and the crystals dissolved. The solution was then warmed briskly with bone black, and filtered. From the filtrate, which was colorless, nothing but rhombic crystals having seven molecules of water of crystallization could be obtained, although a gre-

many variations in the conditions were tried. Analysis of these last crystals was as follows:

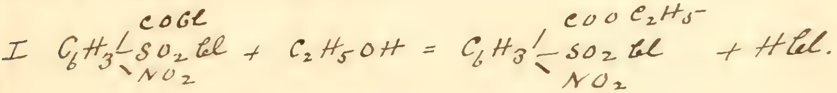
0.2400 gram lost 0.035 gram at 210°
and gave 0.0637 gram $BaSO_4$

| Cal. for $(C_{13}H_8O_6NS)_2Ba + 7H_2O$. | Found |
|---|---|
| $H_2O = 14.40$ | $14.58$ |
| $Ba = 18.29$ | $18.27$ |

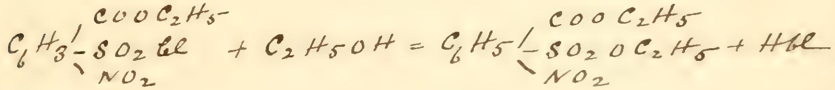
Hollis states that treatment with boneblack decomposes this salt, and hence he did not purify it prior to crystallization. From the experiments just described it seems probable that the impurities present affect the crystalline habit, and the degree of hydration of this salt in a very striking manner. By careful warming with boneblack no decomposition was observed, and the crystals so obtained have constantly seven molecules of crystal water.

## VI. The Action of Alcohols upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

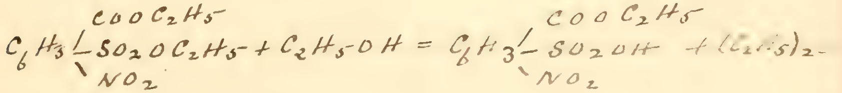
Kastle[1] found that when the chlorides of paranitroorthosulphobenzoic acid (which he supposed to be an individual) were dissolved in alcohol, and the solution boiled for some time, the acid etherial salt of paranitroorthosulphobenzoic acid was the final product. The reactions were shown to be:

I 

$$C_6H_3\begin{array}{l}COCl\\SO_2Cl\\NO_2\end{array} + C_2H_5OH = C_6H_3\begin{array}{l}COOC_2H_5\\SO_2Cl\\NO_2\end{array} + HCl.$$

II 

$$C_6H_3\begin{array}{l}COOC_2H_5\\SO_2Cl\\NO_2\end{array} + C_2H_5OH = C_6H_5\begin{array}{l}COOC_2H_5\\SO_2OC_2H_5\\NO_2\end{array} + HCl$$

III. 

$$C_6H_3\begin{array}{l}COOC_2H_5\\SO_2OC_2H_5\\NO_2\end{array} + C_2H_5OH = C_6H_3\begin{array}{l}COOC_2H_5\\SO_2OH\\NO_2\end{array} + (C_2H_5)_2-$$

Kastle, it will be observed, gave the sym-

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[1] Am. Ch. Journ. XI - 281.

metrical formula to this mixture of chlorides. Several acid etherial salts were made, and a series of the neutral salts of various metals described by him.

The action of pure symmetrical chloride was studied in the same general manner to see if the resulting products would be the same as those formed from the mixed chlorides.

### 1. Action of methyl alcohol upon the Symmetrical chloride.

A portion of the chloride was dissolved in methyl alcohol, and the solution boiled until a drop added to cold water gave no precipitate, of unchanged chloride. The alcohol was then distilled off, and the thick syrup remaining diluted with water. This solution was neutralized with barium carbonate and filtered. On cooling,

the barium salt crystallized in shining mica-like plates, or in yellowish needles corresponding accurately with those described by Kastle. They gave the following analytical results.

0.2664 gram lost 0.0211 gram at 150°, and gave 0.0870 gram $BaSO_4$.

| Cal. for $\left[C_6H_3\begin{matrix}COOCH_3\\SO_2O\\NO_2\end{matrix}\right]_2Ba+3H_2O$ | Found |
|---|---|
| $H_2O = 7.59$ | 7.88 |
| [anhydrous salt] Ba = 20.85 | 20.85 |

2. In like manner the barium ethyl salt was made. It also agreed perfectly with Kastle's description, crystallizing in fine, colorless needles, forming in tufts from a not too concentrated solution. In case it is necessary to concentrate these solutions, it is of advantage to add a small quantity of alcohol to the solution

as this prevents any great amount of saponification, which otherwise takes place to a noticeable extent.

Analysis.

I. 0.2824 gram lost 0.0276 gram at 180° and gave 0.0860 gram $BaSO_4$

II 0.2655 gram lost 0.0262 gram at 190° and gave 0.0815 gram $BaSO_4$.

| Cal. for $\left[C_6H_3\begin{cases}COOC_2H_5\\SO_2O\\NO_2\end{cases}\right]_2Ba+4H_2O$. | Found. | |
|---|---|---|
| | I | II |
| $H_2O$ = 9.51 | 9.77 | 9.86 |
| Ba = 20.00 | 19.84 | 20.02 |

---

Kastle also found that by dissolving the mixed chlorides in alcohol in the cold, and allowing the solution to evaporate, there separated after a time, crystals of the chloride of the acid ethereal

salt of paranitroorthosulphobenzoic acid whose formation and composition is represented in equation I.

This same product was sought for when pure symmetrical chloride was employed, but without success. In every case, crystals of unchanged chloride separated, or else it was found that it had been completely converted into the acid etherial salt. In another trial cold water was carefully added in small portions, since Kastle found that such treatment facilitated the separation of the substance; the chloride alone appeared. Still other attempts were made to obtain the substance by adding a large amount of water to the solution of the chloride

in alcohol, after it had stood for some time. In this way, quite a precipitate was thrown down, and this was filtered off and crystallized from ether. It always proved to be the symmetrical chloride, and none of the other substance was obtained.

Karslake[1] in working with the symmetrical chloride of orthosulphobenzoic acid, was unable to isolate the analogous compound, although from the mixed chlorides, by the action of alcohols, Remsen and Dohme[2] had obtained chloro-ethereal salts.

In as much as the pure symmetrical chloride is relatively stable in cold alcohol (it can be crystallized from

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[2] Am. Ch. Journ. XI, 341.
[1] Inaug. Diss. J. H. Univ. 1895.

warm alcohol with very little loss), it is possible that it is more stable than the chloro etherial salt, and that in consequence the latter, when formed, yields more readily to the further action of alcohol than does the unacted on chloride. Hence when the action begins, it at once proceeds to the limit. The fact that the symmetrical chloride is rather sparingly soluble in cold alcohol, making the use of concentrated solutions impossible, may also be a factor in the case. Whatever may be the cause, this substance could not be obtained under any conditions that were devised.

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Having in my possession a very

small specimen of crystallized unsymmetrical chloride, it was submitted to the action of Ethyl alcohol, under as nearly as possible the conditions employed by Kastle. Crystals of a colorless substance were obtained, which in every respect agreed with Kastle's description of the chloride of the acid Ethyl ethereal salt of paranitro-orthosulphobenzoic acid. Crystallized from ether they melted at 68°.

The conditions employed by Kastle in preparing the chloride would undoubtedly lead to a relatively large proportion of unsymmetrical chloride, and it is to this chloride that the formation of the chloro ethereal salt is apparently due.

# VII. The Action of Phenols upon the Symmetrical Chloride of Paranitroörthosulphobenzoic Acid.

Remsen and Saunders[1] in their investigation of the chlorides of orthosulphobenzoic acid, studied the action of phenol upon these substances, and from both the symmetrical chloride and the mixed chlorides, they obtained a normal diphenyl ether together with a red substance which was not further studied. It was formed in small quantity and was probably the corresponding sulphonphthalein. Later McKee[2] obtained these same substances from both the symmetrical and the unsymmetrical chlorides. R. Meyer[3] obtained analogous substances

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[1] Am. Chem. Journ. XVII 347

[2] Ibid XVIII, 798

[3] Ber XXVI 204

by the action of various phenols upon phthalyl chloride. It seemed probable, therefore, that the chlorides of paranitro-orthosulphobenzoic acid would yield similar derivatives, and a study was accordingly made of the reaction of the symmetrical chloride with a series of phenols. The products in some instances were exceedingly difficult to deal with, possessing properties that made it impossible to prepare them for analysis, but even in such cases there could be little doubt as to the general nature of the reactions which had occurred.

## 1. The Action of Phenol upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

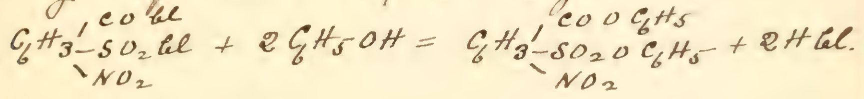
A portion of the symmetrical chloride was brought together with somewhat more than double the molecular amount of phenol. The mixture was placed in a good-sized test-tube and the temperature gradually raised by means of a sulphuric acid bath.

As soon as the phenol melts, some slight action occurs, as is indicated by the fact that the mixture assumes a bright red color. No appreciable amount of hydrochloric acid gas is evolved however, until the liquid mixture has reached a temperature of about 115°. At this point the gas is freely evolved, and the action is complete at a temperature of 125° The temperature observations were made

by means of a thermometer used as a stirring rod in the mixture. During the heating, the color of the liquid becomes a much more intense red, growing darker in shade, and the liquid itself becomes somewhat viscous but does not solidify while hot.

When cool, the melt was repeatedly extracted with boiling water, the aqueous solution being very deep purple in color. The colored matter was removed very slowly in this manner, and so the process was continued with dilute alkali. A solid insoluble residue was thus obtained, of a light brownish color. This was dissolved in alcohol, boiled with boneblack and filtered. On cooling, needles of a straw yellow color were deposited from the alcoholic solution

These proved to be the normal diphenyl etherial salt of paranitroorthosulphobenzoic acid, the formation of this substance being expressed by the equation:



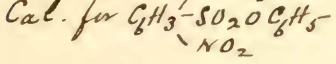
$$C_6H_3\overset{COCl}{\underset{NO_2}{-SO_2Cl}} + 2C_6H_5OH = C_6H_3\overset{COOC_6H_5}{\underset{NO_2}{-SO_2OC_6H_5}} + 2HCl.$$

Analysis of the substance gave the following results:

I. 0.1627 gram gave 0.3398 gram $CO_2$ and 0.0510 gram $H_2O$

II. 0.1999 gram gave 0.4180 gram $CO_2$ and 0.0600 gram $H_2O$

III. 0.2649 gram gave 0.1561 gram $BaSO_4$



Cal. for $C_6H_3\overset{COOC_6H_5}{\underset{NO_2}{-SO_2OC_6H_5}}$ Found.

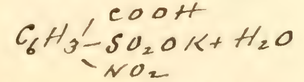
| Cal. | I | II | III |
|---|---|---|---|
| C = 57.14 | 56.97 | 57.03 | — |
| H = 3.26 | 3.47 | 3.33 | — |
| S = 8.02 | — | — | 8.09 |

This substance melts at 119° (uncorr.).

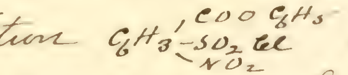
It possesses properties similar to those of the diphenyl etherial salt of orthosulphobenzoic acid described by Saunders. It is insoluble in water, and is unaffected by hydrochloric acid or aqueous alkali. On heating for a short time with alcoholic potash, the needles were transformed into a voluminous precipitate. This was filtered off, dissolved in water, and hydrochloric acid was added. On cooling, characteristic crystals of the acid potassium salt of paranitro-orthosulphobenzoic separated.

Analysis.

0.1392 gram lost 0.009 gram at 150° and gave 0.0385 gram $K_2SO_4$

Cal. for 
$C_6H_3\begin{cases}COOH\\SO_2OK\\NO_2\end{cases}+H_2O$ Found.

$H_2O = 5.95$. $K = 13.65$ $H_2O = 6.51$ $K = 13.35$

No attempt was made to isolate the corresponding intermediate chlor-ethereal salt of the composition  $C_6H_3 \begin{array}{l} COOC_2H_5 \\ SO_2Cl \\ NO_2 \end{array}$ or its amid as was done by McKee[1] in his work on the analogous ethereal salt of orthosulpho benzoic acid.

On evaporating the aqueous extract from the original melt almost to dryness on the water-bath, there was a deposit on the sides of the dish of scales possessing a beautiful bronze-green metallic lustre. They formed a deep purple solution in alkalis, or magenta, if the solution was very dilute, and orange-yellow in acids. On acidifying the alkaline extract with hydrochloric acid, this same substance was precipitated as a brownish flocculent precipitate. It was, however, found to

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[1] Am. Ch. Journ. XVIII - 799

be impossible to obtain this substance in pure condition. The amount formed in the reaction is small, and its properties were such as to render work with it very difficult. The method of precipitation is not satisfactory because, owing to the fact that the substance is soluble in acid solutions to an unusual extent for substances of this class, the solution had to be concentrated to such a degree as to render the precipitated substance very impure from acids and alkali salts. These could not be removed by washing, obviously, without again dissolving the substance. From its properties however, and its color reactions, there can be little doubt that the substance is a sulphonphthaleïn, and that it is always formed in considerable

quantities in the reaction of phenol upon the symmetrical chloride.

It was noticed that the aqueous extract of the ~~salt~~ mass left after fusion was almost always decidedly acid in reaction, and it was thought that this might be due to the formation of an acid etherial salt, whose formation would be expressed by the equations:

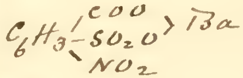
$$C_6H_3\begin{array}{l} / COCl \\ - SO_2Cl \\ \backslash NO_2 \end{array} + C_6H_5OH = C_6H_3\begin{array}{l} / COOC_6H_5 \\ - SO_2Cl \\ \backslash NO_2 \end{array} + HCl$$

$$C_6H_3\begin{array}{l} / COOC_6H_5 \\ - SO_2Cl \\ \backslash NO_2 \end{array} + H_2O = C_6H_3\begin{array}{l} / COOC_6H_5 \\ - SO_2OH \\ \backslash NO_2 \end{array} + HCl.$$

Accordingly the solution was saturated with barium carbonate, the excess of carbonate removed by filtration, the filtrate concentrate; and allowed to cool. Crystals in the form of pearly scales separated, which upon analysis

proved to be the neutral barium salt of paranitroorthosulphobenzoic acid.

0.2291 gram anhydrous salt gave .1386 gram $BaSO_4$



| Cal. for $C_6H_3\begin{array}{l}\diagup\begin{array}{l}COO\\ -SO_2O\end{array}\!\!>Ba\\ \diagdown NO_2\end{array}$ | Found |
|---|---|
| $Ba = 35.85$ | 35.57 |

This would seem to indicate that the reaction is an incomplete one even in the presence of excess of phenol. No indications of the formation of an acid ethereal salt was observed.

## 2. The Action of Orthocresol upon the Symmetrical Chloride of Paranitro-orthosulphobenzoic Acid.

With orthocresol the reaction proceeds with more difficulty. A higher temperature was required (135°-145°), and quite an amount of tarry material was obtained from which very little could be extract. The product was warmed repeatedly with dilute alkali, the solution so obtained neutralized with hydrochloric acid, and distilled with steam for several hours to free it from cresol. The resulting solution was then evaporated to small volume, and acidified with hydrochloric acid. A considerable precipitate was thrown down, which was easily filtered off and dried. In this condition it a dark

purple-red powder, lumps of which possessed a yellowish bronze metallic lustre. In dilute alkaline solution it forms a deep bluish purple solution, while in acids it is crimson, or light yellow if the solution is dilute. It is an excellent indicator, espicially with ammonia.

In the insoluble tarry substance the etherial salt was sought for and obtained in small quantity only. As this ~~entire~~ substance is soluble in alcohol, and separates again on cooling in much the same condition, the etherial salt could not be isolated by crystallization from this solvent. By boiling the substance with benzene, purifying the filtrate with boneblack, and allowing the benzene to evaporate, an almost colorless gummy substance

was obtained, which ~~on~~ when dissolv~~ing~~ed in alcohol, crystallizes in small colorless needles which melt at 89°-90°. They were not obtained in quantity sufficient for analysis, but there was little doubt that they were crystals of the di-ortho-cresol ethereal salt.

Apparently much more decomposition occurred in this reaction than when para cresol was employed, probably in consequence of the higher temperature required for the reaction.

## 3. The Action of Paracresol upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

This reaction was conducted in the same manner as with phenol. No hydrochloric acid was evolved until a temperature of about 110° was reached, although after melting, the solution had steadily darkened to a deep reddish brown color. At 130°, after heating for several hours, hydrochloric acid ceased to be evolved, The product was treated as in the last experiment. The alkaline extract did not exhibit any marked color reactions, such as were observed in most of these experiments, being dull reddish brown in both acid and alkaline solution.

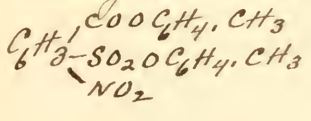
The insoluble residue crystallized from

alcohol in light brown transparent crystals, which did not lose their color by repeated crystallization, and boiling with boneblack, and melted sharply at 117°. From benzene they crystallized in colorless needles or flat, narrow plates. These become opaque on exposure to the air, apparently through loss of benzene of crystallization.

Analysis of the needles from alcohol gave the following results:

I 0.2372 gram of substance gave 0.5137 gram $CO_2$ and 0.0965 gram $H_2O$.

II 0.2223 gram gave 0.1203 gram $BaSO_4$

Cal. for 
$C_6H_3\begin{cases} COOC_6H_4.CH_3 \\ SO_2OC_6H_4.CH_3 \\ NO_2 \end{cases}$

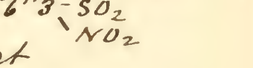
| Cal. | Found. I | Found. II |
|---|---|---|
| C = 59.08 | 59.06 | |
| H = 3.98 | 4.52 | |
| S = 7.49 | | 7.43 |

### 4. The Action of Hydroquinone upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

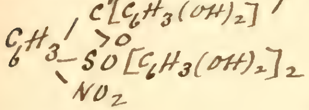
Action with hydroquinone occurs at 120°-135° the mixture at the same time becoming dark colored and viscous. On cooling, the product was powdered and treated with dilute alkali. It readily dissolved, without residue, forming a dark red solution. In concentrated solution the addition of acid produces a voluminous precipitate, dark brown in color, which when washed, and dried in paper forms an almost black powder. A dilute solution of this powder is dark red when alkaline, orange-yellow when acid.

From the way in which this powder

was obtained, and owing to the fact that its solubility prevented repeated washing, it was evident that it would not give close analytical results for a calculated formula. It was thought however, that analysis would give a general idea of the composition.

Analysis of different specimens gave results for sulphur which averaged about 5.5%. The percentage required for the formula  $C_6H_3\begin{array}{l}/C[C_6H_3(OH)_2]_2\\ \;\;>O\\ -SO_2\\ \backslash NO_2\end{array}$ which represents the simplest sulphonfluorescein, is 7.43

The compound could hardly have been so far from pure as to occasion such a discrepancy in results as this. It would appear, therefore, that more than two molecules of hydroquinone enter into reaction with one molecule

of the chloride. Should four molecules be involved in the reaction, leading to a compound of some such formula as  $C_6H_3\begin{array}{l} /\,C[C_6H_3(OH)_2] \\ \quad >O \\ -SO[C_6H_3(OH)_2]_2 \\ \backslash\,NO_2 \end{array}$ the theoretical percentage of sulphur would be 6.00 which corresponds much more closely with the results obtained.

This is in accord with the observations of a number of workers in this laboratory - Lyman, Gilpin, Linn and others - who have worked on various sulphonfluoresceins, and have found that in many cases four, six and even eight phenol residues condense with one molecule of the anhydrous acid. Lyman[1] especially describes a tetra hydroquinone sulphonfluorescein derived from orthosulphoparatoluic acid. No etherial salt was observed.

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[1] Am. Chem. Journ. XVI - 525

## 5. The Action of Resorcin upon the Symmetrical Chloride of Paranitro-orthosulphobenzoic Acid.

The reaction of resorcin with the chloride is a much cleaner one and procede more easily than in the case just described, leading apparently to an individual compound which is well characteryed. During the reaction, which is complete at 125°, the mixture becomes almost perfectly solid, and when cool, it is quite brittle. It was reduced to a reddish powder in a mortar and dissolved in sodium hydroxide, there being no insoluble residue. By the addition of hydrochloric acid, the sulphonfluorescein was thrown down as a chocolate-brown precipitate, which was filtered off, washed to neutral reaction

on a filter, and dried on paper. In this condition it is a light chocolate-brown powder. In dilute alkaline solution it possesses a slight fluorescence being pink by transmitted and yellow by reflected light suggesting Eosin in a general way. It is interesting to note that the sulphon fluoresceïn of orthosulphobenzoic acid possesses a fluorescence that can hardly be distinguished from ordinary fluoresceïn and that the introduction of a nitro group into the acid residue produces much the same effect as do the four bromine atoms in Eosin. In acid solution the color is reddish-orange.

Analysis of the compound, prepared as above described gave the following results

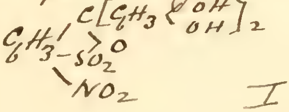
I. 0.1745 gram gave 0.3339 gram $CO_2$ and 0.059 gram $H_2O$

II. 0.1467 gram gave 0.2820 gram $CO_2$ and 0.0432 gram $H_2O$

III. 0.1732 gram gave .3345 gram $CO_2$ and 0.0571 gram $H_2O$

IV. 0.2000 gram gave 0.1104 gram $BaSO_4$

V. 0.1505 gram gave .0820 gram $BaSO_4$

Cal. for  $C_6H_3\left\{\begin{array}{l} C[C_6H_3\{{}^{OH}_{OH}]_2 \\ \quad >O \\ SO_2 \\ NO_2 \end{array}\right.$ Found

| | I | II | III | IV | V |
|---|---|---|---|---|---|
| C = 52.66 | 52.18 | 52.42 | 52.67 | — | — |
| H = 3.46 | 3.76 | 3.27 | 3.66 | — | — |
| S = 7.39 | — | — | — | 7.57 | 7.48 |

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An effort to obtain the anhydride was unsuccessful. Some loss of weight was observed, but the compound underwent decomposition before this loss amounted to much.

## 6 The Action of Pyrogallol upon the Symmetrical Chloride of Paranitro-orthosulphobenzoic Acid.

The product of this action dissolves readily in dilute sodium hydroxide without residue, producing a very deep purple black color when concentrated, passing to grayish violet as the solution is diluted. On adding hydrochloric acid, precipitation occurs, ~~as~~ in most of these reactions. On attempting to filter off this precipitate it forms a sticky black mass on the filter with which little can be done. It is best to evaporate to dryness before filtration and powder the residue. This powder can then be washed fairly clean from alkali salts and acid.

nothing to suggest the formation of an etherial salt was observed.

Analysis of this product for Sulphur showed that in this gallein, as in the case of the hydroquinone phthalein more than two pyrogallol residues had entered the acid residue. The indications were that six had entered into one of the chloride. This also agrees with the observation of Lyman[1], who describes a hexa-pyrogallol gallein of orthosulpho-paratoluic acid.

Probably a mixture of varying composition was obtained, and little importance was attached to the results save as they showed that no etherial salt is formed in the reaction

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[1] Am. Ch. Journ. XVI - 537.

### 7. The Action of β-Naphthol upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

It was hoped that here, as in the case of the monohydroxy phenols an ethereal salt would be obtained. It was found however that very little action occurred, save such as was indicated by the development of a bright carmine color in the melted mixture, until a temperature of about 160° was reached. At this point hydrochloric acid was evolved, but the chloride itself undergoes decomposition. Nothing definite could be isolated among the reaction products, save unchanged β-Naphthol.

# VIII. The Action of Aniline upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

As has been pointed out in the Introduction, it was in connection with the aniline derivatives of ortho-sulphobenzoic acid, that the isomerism of the chlorides was first noticed, two anilids being obtained. Accordingly, when Gray began his study of the chlorides of paranitroorthosulphobenzoic acid, his first effort was to obtain evidence of the existence of two anilids. These were not obtained, however, until after the chlorides themselves had been isolated, as their properties made their isolation and preparation a matter of difficulty.

Some points still remained in doubt

after Gray's study, and a further investigation was thought to be desirable to clear these up.

Some time was spent in an endeavor to obtain a method by which a good yield of fusible, or symmetrical, anilid could be obtained. The yield in all cases tried, is not a good one. The presence of the nitro group appears to complicate the reaction, leading to secondary reactions whose course could not be followed. Upon bringing aniline and the chloride together, a very vivid red color was always observed, and the same was true when it was necessary to employ alkali. The fact that such colors develop when nitro compounds are treated with alkali has been noticed in many instances, and some pro-

gress has been made in the study of these compounds. Jackson and Ittner[1] have lately reviewed this subject.

If a solution of the symmetrical chloride in ether is slowly added to a similar solution of aniline, no appreciable amount of heat is evolved. If the resulting solution is allowed to stand at ordinary temperatures, action proceeds very slowly, aniline hydrochloride being precipitated as the reaction proceeds. This can be filtered off from time to time and the rate of action so observed. In such a way it was found that five grams of chloride required about fifty hours time to react completely with an excess of aniline. Similar results were obtained with chloroform as the solvent.

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Am. Chem. Journ xix-198

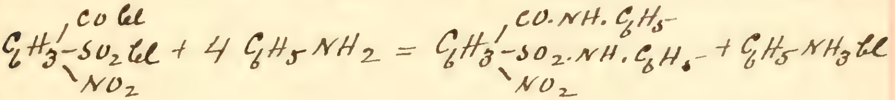
By boiling the solution for an hour or more the reaction is complete.

The method employed was to bring the chloride and an excess of aniline — somewhat more than four molecules — together in chloroform solution. The flask was then boiled for about an hour, when the chloroform was distilled off. During the boiling as well as the distillation more or less bumping occurs in consequence of the aniline hydrochloride which separates and constant shaking of the flask is sometimes necessary. The residue which is in a thick gummy condition in consequence of the presence of an excess of aniline, was digested with water acidulated with hydrochloric acid. The excess of aniline

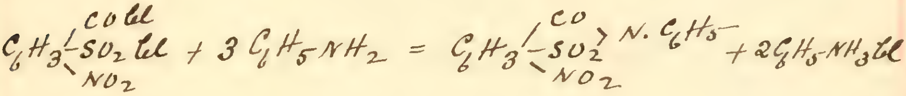
is thus removed and the reaction product obtained as a reddish-brown solid substance. This was treated with dilute sodium hydroxide, all lumps being broken up with a stirring rod. The undissolved substance is largely anil, which was filtered off. The anilid was then regained by acidifying the alkaline solution, in which it was dissolved. It separates immediately as a curdy colorless precipitate, though it is frequently colored pink by impurity. It was found that this color could be removed, in case not much was present, by redissolving the anilid in alkali, and slowly pouring the solution into an excess of dilute acid.

In all cases a considerable amount

of anil was obtained, even when the substances were employed in the molecular ratios of 1:10. The reactions involved, so far as the formation of anilid and anil are concerned, are,



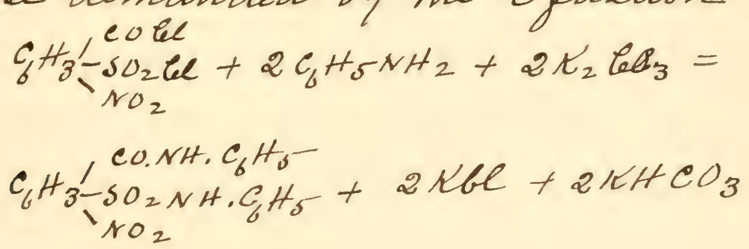
$$C_6H_3\begin{cases}CO\,Cl\\SO_2Cl\\NO_2\end{cases} + 4\,C_6H_5NH_2 = C_6H_3\begin{cases}CO.NH.C_6H_5\\SO_2.NH.C_6H_5\\NO_2\end{cases} + C_6H_5NH_3Cl$$



$$C_6H_3\begin{cases}CO\,Cl\\SO_2Cl\\NO_2\end{cases} + 3\,C_6H_5NH_2 = C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\phantom{x}\left.\begin{matrix}CO\\SO_2\end{matrix}\right>N.C_6H_5 + 2C_6H_5NH_3Cl$$

On the whole the reaction seemed to be the most satisfactory in chloroform solution, the main objection being, that, owing to the simultaneous presence of chloroform, alkali, and a trace of aniline, phenyl isocyanide is always formed, and renders the work more or less unpleasant.

A number of experiments were also made to see if the yield could be increased by employing a modification of the "Schotten-Baumann Reaction"[1] for the formation of anilids. For this purpose an etherial solution of the chloride was added to a like solution of aniline in which was suspended finely powdered anhydrous potassium carbonate. The proportions of the substances were those demanded by the equation



$$C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases} + 2C_6H_5NH_2 + 2K_2CO_3 =$$

$$C_6H_3\begin{cases}CO.NH.C_6H_5\\SO_2NH.C_6H_5\\NO_2\end{cases} + 2KCl + 2KHCO_3$$

Very little anilid was however obtained, but in its place a substance soluble in water, of acid reaction capable of forming salts and yielding

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[1] Ber. XVII - 2545; XXIII, 3430.

several well characterized derivatives. I hope to investigate this reaction more fully at some future time.

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The anilid is rather sparingly soluble in alcohol, from which it is deposited on cooling in very small needles. These melt, as stated by Gray at 222°. It is also soluble in chloroform and glacial acetic acid, but does not form well defined crystals from any solvent. It dissolves in dilute alkali from which solution acids precipitate it unchanged.

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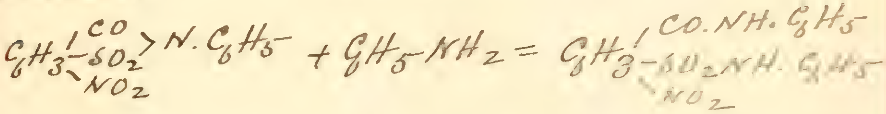
The anil is also soluble in alcohol glacial acetic acid &c. It crystallizes in much better-formed crystals than does the anilid. These melt at 125-

On boiling the anil with aniline for a time it is converted into the anilid

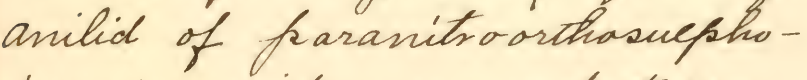


$$C_6H_3\begin{matrix}/CO\\-SO_2\\ \backslash NO_2\end{matrix}\!\!>N.C_6H_5 + C_6H_5NH_2 = C_6H_3\begin{matrix}/CO.NH.C_6H_5\\-SO_2NH.C_6H_5\\ \backslash NO_2\end{matrix}$$

In none of these reactions was any infusible anilid observed.

## IX. The Action of Phosphorus Oxychloride upon the Fusible Anilid.

Hunter[1] found that when either of the anilids of orthosulphobenzoic acid were treated with phosphorus oxychloride, or similar dehydrating agents, a molecule of water was abstracted with the formation of a new substance. A careful study of the compound led to the belief that it was a dianil, and that its formation and structure could be represented by the equation



$$C_6H_4\Big\langle{}^{CO.NH.C_6H_5}_{SO_2NH.C_6H_5} = C_6H_4\Big\langle{}^{C=N.C_6H_5}_{SO_2}\Big\rangle.N.C_6H_5 + H_2O.$$

A corresponding study of the fusible anilid of paranitroorthosulphobenzoic acid was undertaken.

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[1] Am. Ch. Journ. XVIII - 810.

The method employed in this study was as follows. A tubulated retort of convenient size was fused onto the inner tube of a small condenser. This was done to avoid connections, which are nearly always attacked by the oxychloride. Another satisfactory plan is to have the neck of the retort of the same size as the inner tube of the condenser. The ends are placed in contact, and the tubes bound in position by wrapping with asbestos paper. Over the joint so made, a tight rubber tube is drawn.

A convenient amount of phosphorus oxychloride (50 c.c.) was placed in the retort and the anilid (5 gr.) added through the tubulus. An

boiling, with the condenser inverted, the anilid soon dissolved, with evolution of hydrochloric acid gas, and the solution became bright yellow in color, sometimes inclining to orange. The boiling was continued as long as hydrochloric acid was given off. The oxychloride was then distilled off under diminished pressure care being taken to shake the retort constantly during the distillation as violent bumping is almost sure to occur especially towards the end of the operation. The product remaining, spattered over the walls of the retort, was a greenish yellow solid. Water was then added, and the whole allowed to stand for an hour so to thoroughly dissolve the phos-

phoric acid formed in the reaction.

In case the anilid is not perfectly dry, a much more energetic reaction occurs, and on distilling off the oxychloride, the product remains as a dark gummy mass. This should be spread out on the sides of the retort while still liquid. On cooling and adding water, this gum gradually disappears, and in its place is found the yellow solid product just described. The gum appears to be a solution of this substance in phosphoric acid.

After the substance is filtered off and dried, it can be crystallized from acetone, benzene, glacial acetic acid or alcohol. From these solvents it crystallizes in small yellow needles resembling quinone in appearance

The crystals obtained from acetone are rather larger than those from the other solvents, and are more nearly orange in color, apparently because of their greater compactness. When glacial acetic acid is used, care must be taken to avoid any unnecessary heating, as continued heating produces a change that will presently be described. The substance melts at 208°.

Analysis of the substance revealed as follows.

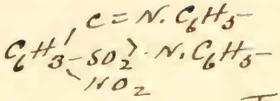
I. 0.3822 gram gave 0.8334 gram $CO_2$ and
0.1272 gram $H_2O$.

II 0.2645 gram gave 0.5812 gram $CO_2$ and
0.0910 gram $H_2O$.

III. 0.2023 gram gave 0.1283 gram $BaSO_4$.

IV 0.2061 gram gave 0.1280 gram $BaSO_4$.

V 0.1853 gram gave 16.73 c.c. N (Standard).

Cal. for 

$C_6H_3\begin{cases} C=N.C_6H_5- \\ SO_2\rangle \cdot N.C_6H_5- \\ NO_2 \end{cases}$

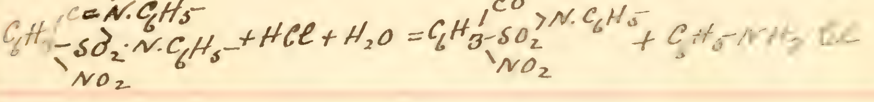
| | | Found. | | | | |
|---|---|---|---|---|---|---|
| | | I | II | III | IV | V |
| C = | 60.11 | 59.47 | 59.93 | – | – | – |
| H = | 3.44 | 3.69 | 3.82 | – | – | – |
| S = | 8.45 | – | – | 8.70 | 8.52 | – |
| N = | 11.08 | – | – | – | – | 11.35 |

For analyses I & II I am indebted to Mr. Nakaseko, who kindly made them for me.

# X. The Action of Reagents upon the Dianil of Paranitroorthosulphobenzoic Acid.

## 1. The Action of Hydrochloric Acid on the Dianil

When the dianil is boiled for some time with concentrated hydrochloric acid the yellow color of the substance disappears and the dianil is converted into a colorless substance without, however, passing into solution. The substance so obtained was filtered off and crystallized from alcohol. It crystallized in small colorless needles, which melted at 183°, and possessed all the properties of the anil, which, in fact, it proved to be. The reaction was therefore



$$C_6H_3\begin{cases}C=N.C_6H_5\\ SO_2.N.C_6H_5\\ NO_2\end{cases} + HCl + H_2O = C_6H_3\begin{cases}\left.\begin{matrix}CO\\ SO_2\end{matrix}\right> N.C_6H_5\\ NO_2\end{cases} + C_6H_5NH_2.HCl$$

This reaction also explains the fact that some anil was always obtained in making the dianil from the anilid. Hydrochloric acid is formed in the reaction, and in turn acts on [illegible] dianil in the sense of the equation just given.

## 2. The Action of Alcoholic Potash on the Dianil.

On boiling the dianil with alcoholic potash for a time, the solution turned red, and nothing but tarry products were obtained. In this respect the dianil differs from the dianil of orthosulphobenzoic acid, which under similar conditions, is transformed into infusible anilid. This observation is, however, in keeping with the fact that the nitro

derivative, is in general much less stable in the presence of alkali.

### 3. The Action of Glacial Acetic Acid on the Dianil.

When the dianil is boiled with glacial acetic acid for some time, the color of the solution changes to a much lighter shade of yellow, or becomes colorless. On evaporating the solution to small volume, and allowing it to cool, a colorless substance separates. This is infusible anilid. It could not be obtained in crystals from any solvent, but always separated in flakes. It does not melt or undergo change at 340°. Like the fusible anilid it dissolves in dilute alkali, but on acidifying the solution it does not im-

mediately reappear. After standing for some time however, it gradually separates in perfectly pure form. In this particular my observation differs from that of Gray[1] who states that this anilid is decomposed by solution in alkali..

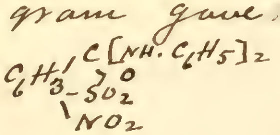
A specimen that had been repeatedly precipitated gave the following results on analysis.

I. 0.1607 gram gave 13.88 c.c. N. (standard)

II 0.2195 gram gave 0.1285 gram $BaSO_4$

III. 0.1357 gram gave .0807 gram $BaSO_4$

Cal. for



$$C_6H_3\begin{cases} C[NH.C_6H_5]_2 \\ \quad >O \\ -SO_2 \\ NO_2 \end{cases}$$

Found.

| | Cal. | I. | II. | III. |
|---|---|---|---|---|
| N = | 10.58 | 10.85 | – | – |
| S = | 8.06 | – | 8.00 | [illegible] |

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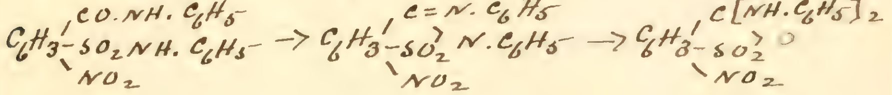
[1] Inaug. Diss. J.H. Univ. 1895.

By this series of transformations it is possible to pass from one anilid to the other, the steps being:



$$C_6H_3\begin{array}{l}/CO.NH.C_6H_5\\ -SO_2NH.C_6H_5\\ \backslash NO_2\end{array} \rightarrow C_6H_3\begin{array}{l}/C=N.C_6H_5\\ -SO_2\rangle N.C_6H_5\\ \backslash NO_2\end{array} \rightarrow C_6H_3\begin{array}{l}/C[NH.C_6H_5]_2\\ -SO_2\rangle O\\ \backslash NO_2\end{array}$$

This is of special interest as affording a means of passing from a derivative of one of the chlorides, to a substance derived from the other, by steps that can be clearly followed.

## Conclusions.

In the course of this ~~preceding~~ investigation several facts have ~~become~~ been established ~~prominent~~.

1. By the methods described, the symmetrical chloride of paranitroorthosulphobenzoic acid can be obtained in fine crystalline form, perfectly free from its isomer, with an average yield of forty percent.

2. By treatment of the chloride with benzene and aluminium chloride, only one chlorine atom can be replaced by a phenyl group.

3. The barium salt of paranitroorthobenzoyl benzenesulphonic acid, when perfectly pure, crystallizes constantly with seven molecules of water of crystallization.

4. With alcohols, the symmetrical chloride yields directly the acid ethereal salt of paranitroorthosulphobenzoic acid, no evidence having been obtained of an intermediate chloro-ethereal salt. The unsymmetrical chloride on the other hand yields the intermediate product.

5. With phenols, two series of derivatives are obtained.

(1) With monohydroxy phenols, both ethereal salts and sulphonphthaleins are formed, the former predominating.

(2) With polyhydroxy phenols no ethereal salts were obtained, but compounds of the unsymmetrical type, usually containing more than two phenol residues.

6. With aniline an anil and an anilid of symmetrical constitution

are formed.

7. With phosphorus oxychloride, the anilid, by loss of water, forms a dianil.

8. This dianil undergoes transformation with

(1) Glacial acetic acid, forming an anilid of unsymmetrical constitution

(2) Hydrochloric acid forming the anil.

(3) Alcoholic potash, with the formation of colored decomposition-products.

# Biographical.

The author of the foregoing dissertation was born at Wilkinsburg Pa, Jan. 29. 1870 Owing to prolonged sickness in childhood his education, prior to entering College, was much interrupted, and was largely confined to instruction received at home.

In the fall of 1887 he entered Wooster University (Ohio), from which institution he received the degree of Bachelor of Arts in 1891. The two following years were spent as a teacher of Sciences in the College of Emporia (Kansas). In 1893 he entered the Johns Hopkins University where he has since been a student of chemistry, with physics and mathematics as subordinate studies.

In 1895 he was appointed University

Scholar in Chemistry. During 1895-6 he served as lecture assistant to Prof. Remsen and Dr. Renouf in the Undergraduate courses. In the spring of 1896 he was appointed Fellow for the present year.